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(19)

(54) FOOD COMPOSITIONS

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E/C 4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to food compositions containing an aqueous phase having a pH of from 3.0 to 5.5.

It is often necessary to give food compositions a heat treatment (pasteurization or sterilization) in order to obtain a product with an acceptable shelf-life. It is also known that for microbiological reasons for neutral products a sterilization treatment is necessary for a long shelf-life, whereas for acid products having a pH below about 4.5 a pasteurization treatment is sufficient for a shelf-life comparable with that of neutral, sterilized products.

However, many food compositions undergo deterioration by sterilization treatments, because for example the emulsion is not stable enough to withstand sterilisation, or off-flavours are formed or proteins are denatured during sterilization. Therefore, in general food compositions having a pH below about 4.5 which need only to be pasteurized are preferable. The difficulty with the latter products is however that often these products have an acid taste which is sometimes not acceptable and/or proteins such as casein are so close to their isoelectric point that they coagulate, which can be undesirable. For instance, a known disadvantage of many commercial mayonnaises is that they taste too acid and other products like pancake batter, margarines, "halvarines" (which are margarine like products containing about 40% fat instead of about 80% fat) whipping creams, and sweet desserts are also unacceptable if they have an acid taste.

It has been found that food compositions containing an aqueous phase having a pH of from 3.0 to 5.5 can now be made, having an improved heat stability and, if certain precautions have been taken, a markedly decreased acid taste despite the low pH of the product. According to the invention such food compositions can be prepared by incorporating into the food composition an effective amount of an isolated complex of a globular protein and an algal anionic polysaccharide, such as sodium alginate and carrageenan, as an essential ingredient.

The present invention provides a food composition comprising an aqueous phase of pH from 3.0 to 5.5, from 0.05 to 10% by weight of the food composition of an isolated complex, of a globular protein and an algal anionic polysaccharide, and a dry matter content, exclusive of the isolated complex, of from 3 to 85% by weight. Preferably the dry matter content, exclusive of the isolated complex, contains at least 70% by weight, of fat, protein, and/or carbohydrate, but can also contain other minor ingredients, such as emulsifiers, common salt and preserving, flavouring and colouring agents. Preferably the complex is one which has been obtained from whey.

In this specification globular proteins are to be understood as proteins which form stable colloidal solutions in water in the whole pH range of 2.0-7.0, if required after addition of salt. Examples of these globular proteins are:

1) the proteins present in whey obtained in the preparation of hard or soft cheeses and quark, and remaining after the isolation of casein from buttermilk, i.e. mixtures of the globular proteins as occurring in milk, e.g. beta-lactoglobulin, alpha-lactalbumin, serum-albumin, immunoglobulins and polypeptides of relatively high

molecular weight,

2) blood serum proteins, the main constituent (about 80%) of which is blood-serum albumin.

3) egg-white proteins, of which the main components are ovalbumin, conalbumin and ovumucoid (J.Sci.Fd.Agri. *17* (1966), 101-111,

4) soya whey proteins,

5) yeast proteins,

6) wheat germ proteins,

7) egg-yolk proteins and similar lipoproteins.

By isolated complex is meant the complex isolated from the aqueous medium (including its dissolved solids) in which the complex is prepared by precipitation.

Some of the complexes to be used in the process according to the invention have been described before. Suitable preparations are the following.

Alginate complexes can be prepared by dissolving an alginate in an aqueous phase, having a pH of about 9 to accelerate dissolving of the alginate, mixing the alginate solution with an adqueous phase containing the globular protein, and adjusting the pH of the mixture to about 3 for optimum precipitation of the complex of alginate and globular protein.

Carrageenan complexes can be prepared by dissolving a carrageenan in an aqueous phase having a pH of about 6.0-6.4 and a temperature of about 60°C while stirring for about 15 minutes, followed by cooling to about 20°C and mixing with an aqueous phase containing the globular protein, and adjusting the pH of the mixture to about 2 for optimum precipitation of the complex of carrageenan and globular protein.

The precipitated complexes can be isolated by centrifuging. If desired, other insoluble ingredients to be present in the final food product can be added to the precipitated complex before the aqueous medium is removed. When the isolated complexes are suspended in water, the suspension can be spray-dried.

Similar processes for the preparation of these complexes are known from the literature, e.g. US patent specifications 3,404,142; 3,069,327; 3,252,961 and 1,732,026.

The ratio of algal anionic polysaccharide/globular protein in the isolated complexes is preferably from 1:2 to 1:7 by weight. The complexes as isolated can contain lactose, for example the complexes, obtained by interacting sodium alginate or carrageenan with whey at a pH or from 2 to 3 followed by centrifuging the precipitate, can contain about 10-20% lactose.

If un-denatured proteins are desired, the complex formation is carried out at a temperature not above 65°C, preferably at room temperature and alginate complexes are then preferable, but carrageenan complexes can also be used. If however heat-denatured globular proteins, for example heat-denatured whey proteins, are used, carrageenan complexes are most suitable and the precipitation process can include a heating step in which the mixture having a pH of from 4.5 to 7.0, preferably about 4.7, is heated at a temperature of about 90-100°C for about 15 minutes. This heating step may be carried out before or after addition of the algal anionic polysaccharide. If such a heat-treatment is used, less algal anionic polysaccharide is necessary for the isolation of the precipitate. However the isolated precipitate contains both heat-denatured globular proteins and a complex of algal anionic polysaccharide and globular proteins. Thus the proportion of complexed globular protein in the precipitate is lower than in the precipitate obtained on complex formation with un-denatured globular proteins.

The isolated complexes are applicable in many types of food compositions both oil-in-water emulsions, such as mayonnaise, liquid pancake batter, creams, dairy products like yoghurt and quark, and water-in-oil emulsions, such as spreads like butter, halvarine and margarine.

The use of isolated complexes of globular proteins and algal anionic polysaccharides in food compositions having a pH of from 3.0 to 5.5 has the following advantages.

a) Proteinaceous by-products from the dairy and meat industries can be isolated and used in the preparation of foodstuffs, so that the discharge of proteins in the industrial effluents, which is not acceptable in view of both the malnutrition and the environmental pollution in the world, is no longer needed.

b) The algal anionic polysaccharides are ingredients which are generally recognized as safe in the preparation of foodstuffs.

c) The food compositions can easily be made microbiologically stable in view of their low pH.

d) When complexes of algal anionic polysaccharides with whey proteins are employed, the ratio of proteins to the lactose and salts in the whey is strongly increased, which has been found to give many of the food compositions according to the invention a taste which is markedly less acid than would have been expected at the low pH, this effect is particularly useful in the pH range of from 3.5 to 5.0; often the products completely lack an acid taste. However, if an acid taste is desired, this can be promoted by incorporating in the food composition an appreciable amount of buffering salts, such as lactates, citrates and acetates. Thus, a particular embodiment of the invention is a food composition in which the level of buffering salts is as low as possible to de-

crease the acid taste of the food composition. This can easily be achieved by taking care that the further ingredients of the food composition do not comprise buffer salts or only a small amount of them.

As stated before, many commercial mayonnaises or similar products are too acid. But this disadavntage is often unavoidable in view of keepability problems. The present invention provides mayonnaises and similar oil-in-water emulsions having the required low pH which is necessary for good keepabilty, but lacking the strong acid taste.

A particular embodiment of the present invention is a food composition suitable for use as a liquid pancake batter which is a new product enlarging the range of convenient foods. Usually pancakes are made by housewives or in restaurants by first admixing a self-raising flour or a ready-mixed flour with water or milk to prepare batter which is then used for baking pancakes. The batter thus prepared has a very limited shelf-life owing to microbiological deterioration and/or physical instability of the product and its preparation is rather time consuming. The present invention provides a liquid pancake batter, comprising from 1 to 5% by weight of the isolated complex, from 25 to 50% by weight of flour, from 1 to 10% by weight of mono-and/or di-saccharides, from 2 to 8% by weight of fat, and from 40 to 70% by weight of water, the total amount of such ingredients being 100%. Batters have been made from water, an isolated complex of un-denatured whey protein and carrageenan, wheat flour, maize oil, whey powder, sodium chloride, sucrose and optionally sodium stearoyllactate and sorbic acid, which were ready for use and had a shelf-life of at least 2 months at 10-20°C. The microbiological stability is obtained by a combination of low pH (below 4.5) and pasteurization. If sorbic acid is added, for example at a level of about 0.1%, even the shelf-life after opening the container is quite acceptable. Owing to the presence of the complexes and a sufficiently low level of buffering salts the product does not taste acid despite the low pH.

The invention also provides a food composition having an aqueous phase of pH from 3.0 to 5.5 and comprising an oil-in-water emulsion, having from 1-5% by weight of the isolated complex, from 3 to 20% by weight of mono-and/or di-saccharides, from 10 to 50% by weight of fat, from 0.3 to 2.0% by weight of edible emulsifier, and from 40 to 85% by weight of water, the total amount of such ingredients being 100%. A particular embodiment is a cream having a pH of about 4.9 and containing about 40% by weight of a fat phase with a poly-unsaturated fatty acid content of more than 30 mole% and about 60% by weight of an aqueous phase in which the protein is introduced in the form of an isolated complex of whey protein and sodium alginate.

The invention further provides a food composition having an aqueous phase of pH from 3.0 to 5.5 comprising a water-in-oil emulsion, having from 1 to 10% by weight of the isolated complex, from 25 to 60% by weight of fat, and from 30 to 70% by weight of water, the total amount of such ingredients being 100%. A particular embodiment is a low calorie fat spread containing about 40% of a fat phase and about 60% by weight of an aqueous phase in which about 6-7% by weight of an isolated complex of a globular protein and an algal anionic polysaccharide is used as the protein source. As fat, both butterfat and margarine fat compositions can be used.

A further embodiment is a low calorie protein spread which is in fact an aqueous suspension of an isolated complex of globular protein and an algal anionic polysaccharide, to which are added a small amount of fat, for example 10% by weight, some additional stabilizing and/or thickening agent, for example 1% by weight of tragacanth, and flavour and colouring agents to modify the flavour of the product in the desired direction, for example a spread having a meat, fish, ginger, orange or paprika flavour. It has been found possible to supplement the isolated complex with uncomplexed heat-denatured whey protein. Such a spread can be used as such on eg. toast or crackers or can be mixed with about half its weight of cold or luke warm milk to form a sauce. Thus the invention also provides a food composition having an aqueous phase of pH from 3.0 to 5.5 suitable for use as a low calorie protein spread, comprising from 1 to 10% by weight of the isolated complex, from 3 to 20% by weight of fat, from 0 to 8% by weight of additional protein, from 0.5 to 2% by weight of nonionic polysaccharide, for example tragacanth, and from 60 to 95% by weight of water, the total amount of such ingredients being 100%.

A commercially very attractive application of the invention is the use of an isolated complex of a globular protein and an algal anionic polysaccharide as a partial substitute for curd in the preparation of quark. Because quark has a weak acid taste of its own, it is not necessary in this embodiment to ensure that the level of buffer salts is rather low. But it is a real advantage both economically and from a nutritional point of view that the whey proteins which are usually discarder by-products in the quark preparation, can now be used in the main product and even without heat-denaturation.

The invention therefore also provides a food composition having an aqueous phase of pH from 3.0 to 5.5, comprising a mixture of quark and the isolated complex in which the isolated complex forms from 10 to 40% of the total dry matter of the food composition.

The invention further provides a process for the preparation of a food composition according to the invention which comprises

a) interacting an algal anionic polysaccharide with a globular protein in an aqueous medium having a pH of from 1 to 4 in order to form a precipitate of a complex of the globular protein and the algal anionic polysaccharide,

b) isolating the precipitate formed from the aqueous medium, and

c) mixing the isolated complex with other food ingredients.

As stated before the method for the preparation and isolation of the complexes has been described before, but the use of a complex of a globular protein and an algal anionic polysaccharide in the preparation of a food composition having an aqueous phase having a pH in the range of 3.0-5.5, particularly 3.5-5.0 has not been described before and it has been found that such use gives unexpected advantages and technical effects.

The invention is illustrated by the following Examples, which show several embodiments of the invention. Amounts, here as in the rest of the specification, are by weight, unless otherwise stated.

EXAMPLE I

A complex of heat-denatured whey protein and carrageenan was made by dissolving 0.1% carrageenan in cheese whey (containing 0.7% whey protein) having a pH of 6.4 and a temperature of 60°C. After adjusting the pH to 4.7 by addition of hydrochloric acid the whey protein was heat-denatured by heating at 95°C for 15 minutes. Then the mixture was cooled to 20°C and further acidified to pH 2. The precipitate was isolated by centrifuging. An aqueous dispersion of the isolated complex containing 2.29% of the complex was made and the pH was adjusted to 4.0. To this dispersion were added 1.25% of cream containing 40% milk fat, 3% maize oil, 0.5% locus bean gum and 0.4% tragacanth while stirring with an ultrasonic stirring apparatus known as Ultra Turrax (Trade Mark). After heating to 60°C the mixture was stirred another 30 minutes. After cooling the product was packaged. The product had a texture which resembles yoghurt, but did not taste acid although the pH was 4.0.

EXAMPLE II

An aqueous dispersion of an isolated complex of un-denatured whey protein and sodium alginate (prepared in a manner similar as described in Example I of US Patent 3,404,142) containing 3.9% complex, 3% protein, was made having a pH of 3.0. To improve the texture of the product this dispersion was made alkaline (pH 9.3) with N caustic soda and again acid (pH 3.9) with N hydrochloric acid. At 60°C 1% tragacanth was added and 10% maize oil was emulsified into the mixture, followed by addition of flavour ingredients, sodium chloride and colouring agent. After heating a further 30 minutes at 80°C (pasteurization of the product), the product was filled into tubs. The low calorie protein spread did not taste acid, although the pH was 3.9, and can be used as such on eg. toast or crackers. A sauce was made from the product by admixing with half its weight of either cold or luke warm milk.

EXAMPLE III

A complex of undenatured whey protein and carrageenan was prepared by dissolving 0.2% carrageenan in cheese whey adjusted at pH 6.4 by stirring for 15 minutes at 60°C. The complex was formed after cooling to 20°C and acidifying to pH 2 with hydrochloric acid. The complex was isolated by centrifuging, redispersing in water and spray-drying the dispersion.

An aqueous suspension of 30 parts of the spray-dried complex containing 30% protein, 16 parts sucrose, 1 part sorbic acid, 6 parts salt and 20 parts whey powder in 556 parts water was heated for 30 minutes at 80°C. After cooling down to 20°C, 322 parts wheat flour and 50 parts maize oil were added. Intensive stirring with an Ultra-Turrax apparatus was continued until a smooth and thin batter was formed. The pH was adjusted to 4.0 with hydrochloric acid and the product was filled into bottles and pasteurized in a Stork (Trade Mark) rotating sterilizer at 55°C for 30 minutes. After storage during 2 months at 10°C no change in baking properties was observed. This liquid pancake batter having a pH of 4.0 can be used as such for baking pancakes which do not taste sour.

EXAMPLE IV

A fat phase of 32 parts maize oil, 8 parts inter-esterified palm kernel oil and 1 part distilled palmitic acid monoglyceride was made at 60°C.

An aqueous phase of 5 parts cream containing 40% milk fat, 5 parts sugar and 49 parts of a suspension of the same complex as used in Example II but containing 2% protein was made at 60°C.

The fat phase was emulsified in the aqueous phase and the emulsion was homogenized and pasteurized.

After storage for 3 weeks at 5°C the cream was whipped within 3 minutes with a normal mixer and had a good rigidity and appearance. Although the pH of the

whipping cream was 4.9, the product did not taste sour.

EXAMPLE V

A water phase having a pH of 4.0, made from 45% water and 55% of an aqueous slurry of an isolated alginate/whey protein complex containing 20% dry matter, was mixed in a conventional manner with a fat phase, in a ratio of 60:40, to form a low calorie water-in-oil emulsion comparable with margarine but containing only 40% fat. Although the pH of the water phase was 4.0, the product had a neutral taste.

EXAMPLES VI to VIII

The procedure of Example III was repeated with the following exceptions:

Example VI:
1) 27 parts instead of 30 parts of spray-dried complex were used;
2) 2.5 parts of sodium stearoyl lactate were added;
3) the pH was adjusted to 4.3 instead of 4.0;
4) the pasteurization was carried out for 30 minutes at 60°C instead of 55°C;
5) the product was stored for 6 weeks at 20°C instead of 2 months at 10°C.

Example VII: 40 parts of a spray-dried complex of wheat germ protein and carrageenan were used instead of a complex of whey protein and carrageenan.

Example VIII: 36 parts of a spray-dried egg yolk protein/carrageenan complex instead of 30 parts of spray-dried whey protein/carrageenan complex were used.

The resulting liquid pancake batters had properties equal to that of Example III.

EXAMPLE IX

The procedure of Example II was repeated with the exception that the dispersion of whey protein/alginate complex was replaced by an aqueous dispersion of an isolated blood serum protein/alginate complex containing 3% protein. The base spread had properties equal to that of Example II.

EXAMPLE X

A base spread wtih a pH of 3.9 was made from 33.3% of an aqueous dispersion of an isolated complex of undenatured whey protein and sodium alginate, similar to that of Example II (having a fat content of 0.3% and a dry matter content of 22.6%); 22.0% heat-denatured whey protein (0.4% fat and 17.1% dry matter); 9.7% maize oil; 1.0% tragacanth; 0.1% sorbic acid and 33.9% demineralized water. By addition of different flavouring and colouring ingredients both sweet and savoury spreads were made.

EXAMPLE XI

In a quark preparation (quark has a pH of 4.6-4.7) which is normally made from 67.5% curd having a dry matter content of about 18.5%, 22% sour whey, 10% sucrose and 0.5% locust bean gum, half of the curd was replaced by a complex of heat-denatured whey protein and carrageenan, prepared as described in Example I, and sour whey giving the following composition: 34% curd; 35.5% sour whey; 20% complex slurry (dry matter 25%); 10% sucrose and 0.5% locust bean gum.

The composition had similar properties as the conventional quark preparation as regards product texture, heat stability, taste and shelf-life for 14 days at 10°C.

WHAT WE CLAIM IS:

1. A food composition comprising:
   a. an aqueous phase of pH from 3.0 to 5.5,
   b. from 0.05 to 10% by weight of an isolated complex as hereinbefore defined of a globular protein as hereinbefore defined and an aligal anionic polysaccharide, and
   c. a dry matter content, exclusive of the isolated complex, of from 3 to 85% by weight.
2. A food composition according to Claim 1, in which the pH is from 3.5 to 5.0.
3. A food composition according to Claim 1 or Claim 2, in which at least 70% by weight, of the dry matter content, exclusive of the isolated complex, is fat, protein and/or carbohydrate.
4. A food composition according to any preceding Claim, in which the isolated complex is one which has been obtained from whey.
5. A food composition according to any one of Claims 1 to 4 and suitable for use as a liquid pancake batter, comprising from 1 to 5% by weight of the isolated complex, from 25 to 50% by weight of flour, from 1 to 10% by weight of mono- and/or disaccharides, from 2 to 8% by weight of fat, and from 40 to 70% by weight of water, the total amount of such ingredients being 100%.
6. A food composition according to any one of Claims 1 to 4, and comprising an oil-in-water emulsion having from 1 to 5% by weight of the isolated complex, from 3 to 20% by weight of mono- and/or disaccharides, from 10 to 50% by weight of fat, from 0.3 to 2.0% by weight of edible emulsifier, and from 40 to 85% by weight of water, the total amount of such ingredients being 100%.
7. A food composition according to any one of Claims 1 to 4 and comprising a water-in-oil emulsion, having from 1 to 10% by weight of the isolated complex, from 25

to 60% by weight of fat, and from 30 to 70% by weight of water, the total amount of such ingredients being 100%.

8. A food composition according to any one of Claims 1 to 4, and suitable for use as a low calorie protein spread, comprising from 1 to 10% by weight of the isolated complex, from 3 to 20% by weight of fat, from 0 to 8% by weight of additional protein, from 0.5 to 2% by weight of nonionic polysaccharide, and from 60 to 95% by weight of water, the total amount of such ingredients being 100%.

9. A food composition according to any one of Claims 1 to 4, comprising a mixture of quark and the isolated complex, in which the isolated complex forms from 10 to 40% by weight of the total dry matter of the food composition.

10. A food composition according to Claim 1, substantially as described in any one of Examples I to V.

11. A food composition, according to Claim 1, substantially as described in any one of Examples VI to XI.

12. A process for the preparation of a food composition as claimed in any preceding claim, which comprises:

a. interacting an algal anionic polysaccharide with a globular protein as hereinbefore defined in an aqueous medium having a pH of from 1 to 4 to form a precipitate of a complex of the globular protein and the algal anionic polysaccharide,

b. isolating the precipitate formed from the aqueous medium, and

c. mixing the isolated complex with other food ingredients.

13. A process according to Claim 12, substantially as described in any one of Examples I to V.

14. A process according to Claim 12, substantially as described in any one of Examples VI to XI.

15. A product which has been prepared by a process according to any one of Claims 12 to 14.

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